

The University of Chicago

THE IONIZATION CONSTANTS
AND HEATS OF IONIZATION OF THE
BISULFATE ION FROM 5° TO 55° C.

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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CURTIS RANDOLPH SINGLETERRY

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This problem was suggested by Professor T. F. Young, whose stimulating interest and suggestions have contributed largely to the outcome of the work. To him, and also to Mr. Irving Klotz, in co-operation with whom the experimental work here reported was done, I wish to express my sincere appreciation.



INTRODUCTION

Measurements of the heat of dilution of sulfuric acid made in this laboratory by Groenier¹ agree with the later data for the dilute region obtained by Lange, Monheim, and Robinson² and with the values of $\bar{L}_2$ for sulfuric acid calculated by Harned and Hamer³ from electromotive force measurements, in requiring a value for the heat of ionization of the bisulfate ion of the order of 5000 calories per mol. The heat of ionization of bisulfate ion at 25°C. derived analytically by Hamer⁴ from electromotive force measurements of cells of another type than that used by Harned and Hamer is, however, 2229 calories per mol, or less than half the value indicated by calorimetric work. This large discrepancy demands further investigation.

Early attempts to evaluate the heat of ionization of the bisulfate ion, or the related change in degree of ionization with temperature, were based upon experimental work of insufficient accuracy. Jones and Douglas⁵ concluded from conductivity measurements at 0°, 15°, 25° and 35°C. that the variation in the degree of ionization of sulfuric acid with temperature was not detectable by their methods. Luther concluded⁶ from an analysis of the conductance and freezing point data available in 1907 that there was no marked temperature coefficient for the ionization constant of bisulfate ion. The earliest significant work is that of Noyes and Eastman,⁷ who measured the conductance of sulfuric acid

¹Groenier, Ph. D. Thesis, The University of Chicago, 1931.

²Lange, Monheim, and Robinson, J.A.C.S., 55, 4733 (1933).

³Harned and Hamer, J.A.C.S., 57, 31 (1935).

⁴Hamer, J.A.C.S., 56, 860 (1934).

⁵Jones and Douglas, American Chemical Journal, 26, 428 (1901).

⁶Luther, Z.f. Electrochemie, 13, 294 (1907).

⁷A. A. Noyes and others, "The Electrical Conductivity of Aqueous Solutions," The Carnegie Institution, Washington, D. C., 1907, pp. 239-81.

in a specially designed cell at temperatures from 18°C. to 218°C. They also studied the conductance of potassium bisulfate solutions at 18°, 100° and 156°C. The ionization constants for the bisulfate ion were calculated from the conductivity data according to the conception of partial ionization of strong electrolytes then prevalent, but the assumption of essentially complete ionization of the first hydrogen of the acid would not have led to greatly different results in the dilute solutions considered. From his calculated values for the ionization constant for the second hydrogen at 18°, 100° and 156°, Noyes¹ computed an empirical equation for the heat of ionization,

$$\Delta H^\circ = 14,170 - 65T \quad (1)$$

where T is the absolute temperature. This equation leads to $\Delta H^\circ = -4750$ calories at 18°C. and $\Delta H^\circ = -5400$ calories at 25°C. Noyes and Eastman also calculated the heat of ionization from the thermochemical data of Thomsen² for the heat of reaction of sodium bisulfate with sodium hydroxide, using their own value for the degree of ionization of the bisulfate ion in the solution Thomsen used. For ΔH° for the ionization of the bisulfate ion they obtained -5020 calories at 18°C.

Muller³ measured the heats of dilution and the conductances of sulfuric acid at 14°, 26° and 38°. From the concepts of the relation between conductivity and degree of dissociation then current he calculated ΔH of ionization for sulfuric acid to be -1,440 calories at 14°C., -4,210 calories at 25°C., and -3,090 calories at 38°C. The calorimetry was done with mercury thermometers. Both temperature and conductance measurements were of insufficient precision to permit satisfactory extrapolations to infinite dilution in the case of a moderately weak electrolyte such as sulfuric acid, although such extrapolations were an essential part of his calculations.

Pitzer,⁴ as a part of a general study of the heats of ionization of weak electrolytes, determined the heat evolved when

¹Ibid., p. 345.

²Thomsen, "Thermochemische Untersuchungen," 1, 100-102 (1882).

³Muller, Bull. Soc. Chim. De France (4) 13, 1053 (1913).

⁴Pitzer, J.A.C.S., 59, 2365 (1937).

0.01 liter of .790 m. sodium sulfate solution was added to 0.875 liter of 1.000 m. hydrochloric acid. From this experiment he calculated ΔH° of ionization for the bisulfate ion to be -5200 ± 500 calories, at 25°C .

Sherrill and Noyes¹ have recalculated the ionization constant for the bisulfate ion at 25° by a method in which they combined the conductance data from Noyes and Eastman with transference data from Noyes and Stewart² to avoid the assignment of an arbitrary value to the mobility of HSO_4^- ion. They assumed complete ionization of the first hydrogen, employed the Debye-Hückel-Onsager theory of the change of ion mobilities with concentration, and utilized individual activity coefficients, based on those published by Lewis and Randall,³ to obtain "true" or thermodynamic dissociation constants. Sherrill and Noyes somewhat arbitrarily chose the average value of K in the concentration range from .0125 to .005 formal for their final value of $K = .0115$ at 25°C . because this range included the most dilute solutions for which they considered the data reliable. Their K, however, shows a definite trend with the concentration, and an extrapolation to infinite dilution such as has become common since that time indicates a value near $K = .010_2$.

The writer applied a similar recalculation to the data of Noyes and Eastman for the conductance of sulfuric acid at 18°C ., arriving at an extrapolated value of $K = .012_7$ comparable with the $K = .010_2$ derived from extrapolation of the Sherrill and Noyes calculations at 25° . Application of the approximate relationship, $\Delta \ln K / \Delta T = \Delta H / RT^2$, to these values indicates an average ΔH° for the ionization of bisulfate ion of $-5,800$ calories in the range from 18° to 25°C . The uncertainty of a heat of ionization calculated from two values of the ionization constant for temperatures so close together is of course large, but it probably does not exceed ± 1000 calories.

Another approach may be made through calculations based upon the activity coefficients for sulfuric acid evaluated by

¹Sherrill and Noyes, J.A.C.S., 48, 1861 (1926).

²Noyes and Stewart, J.A.C.S., 32, 1133 (1910).

³Lewis and Randall, "Thermodynamics," McGraw Hill, 1923, p. 381.

Harned and Hamer¹ from their e. m. f. measurements on mercurous sulfate-mercury and on lead sulfate-lead dioxide electrodes against the hydrogen electrode. The calculations involve the use of the individual activity coefficients calculated by Kielland² from the extended form of the Debye-Hückel equation. His assumptions concerning the ionic diameter term were based in part upon published values for the ionic radii, and in part upon the agreement obtained when mean activity coefficients of strong electrolytes computed from the individual coefficients were compared with the accepted experimental values. Given such individual coefficients, we can compute the ionization constant of the bisulfate ion upon the assumption that the stoichiometrical activity coefficients depart from the individual ones described above simply because part of the hydrogen and sulfate are present as HSO_4^- ions. We adopt the following symbols:

m = molality of sulfuric acid

(H^+) = actual molality of H^+ present at equilibrium

$(\text{SO}_4^{=})$ = actual molality of $\text{SO}_4^{=}$ present at equilibrium

$\gamma_{\pm}$ = stoichiometrical activity coefficient of sulfuric acid

f = individual or Debye-Hückel activity coefficients of the ions

$a_{\text{H}} = f_{\text{H}}(\text{H}^+)$, etc. = activity

$\mu = m + 2(\text{SO}_4^{=})$ = the ionic strength of the solution

It follows from our assumption that

$$\gamma_{\pm}^3 \equiv \gamma_+^2 \gamma_- \equiv \left(\frac{a_{\text{H}^+}}{2m}\right) \left(\frac{a_{\text{SO}_4^{=}}}{m}\right) = \left[\frac{f_{\text{H}^+}(\text{H}^+)}{2m}\right]^2 \frac{f_{\text{SO}_4^{=}}(\text{SO}_4^{=})}{m} \quad (2)$$

or

$$(\text{SO}_4^{=}) = \frac{\gamma_{\pm}^3 \cdot 4 m^3}{f_{\text{H}^+}^2 f_{\text{SO}_4^{=}}(\text{H}^+)^2} \quad (3)$$

$$(\text{HSO}_4^-) = m - (\text{SO}_4^{=}) \quad (4)$$

$$(\text{H}^+) = 2m - (\text{HSO}_4^-) \quad (5)$$

Corresponding values of m and $\gamma_{\pm}$ were taken from the table published by Harned and Hamer and a reasonable value of (H^+) assumed for the first approximation. Values of f_{H^+} and $f_{\text{SO}_4^{=}}$ for the cor-

¹Harned and Hamer, J.A.C.S., 57, 27 (1935).

²Kielland, J.A.C.S., 59, 1675 (1937).

responding ionic strength were read from a graph based on Kielland's table. The value for (H^+) computed by equation (5) was compared with that originally assumed and a probable intermediate value chosen for the next approximation. The process was continued until the assumed (H^+) was identical with that subsequently obtained by equation (5). A numerical sample of the final stage of the calculations for .001 molal H_2SO_4 at $25^\circ C$. is given to illustrate the method.

$(H^+) = 1.8931$, estimated from previous approximation

$\gamma_{H_2SO_4} = .830$, from Harned and Hamer's table

$f_{H^+} = .948$, from Kielland's table

$f_{SO_4^{=}} = .797$ " " "

$f_{HSO_4^-} = .944$ " " "

$$(SO_4^{=}) = \frac{.830^3 \times 4 \times 10^{-9}}{.948^2 \times .797 \times 1.8931^2} = .8934 \times 10^{-3}$$

Resulting $(H^+) = 1.8934 \times 10^{-3}$

Assumed $(H^+) = \underline{1.8931} \times 10^{-3}$

Final average $(H^+) = 1.8932 \times 10^{-3}$

Final $(SO_4^{=}) = .8932 \times 10^{-3}$

Final $HSO_4^- = .1068 \times 10^{-3}$

$$K = \frac{1.8932 \times .8932}{.1068} \cdot \frac{.948 \times .795}{.944} \times 10^{-3} = .01263$$

Values of $(SO_4^{=})$, (H^+) , and (HSO_4^-) were calculated for concentrations of .0005, .001, .002, .005 and .01 m. H_2SO_4 at 0° , 15° , 25° , 40° and $60^\circ C$. For each concentration at each temperature a value of the ionization constant was calculated from the equation

$$K = \frac{(H^+) (SO_4^{=})}{(HSO_4^-)} \frac{f_{H^+} \times f_{SO_4^{=}}}{f_{HSO_4^-}} \quad (6)$$

Kielland's table was again used for the individual activity coefficients. He does not list HSO_4^- ion; the value he published for HSO_3^- , HCO_3^- and $H_2PO_4^-$ was adopted. Temperature corrections were made in the coefficients used for calculations at temperatures other than $25^\circ C$. These corrections were based on the limiting law relationship, $-\log f_{2980}/-\log f' = (DT)^{3/2}/(DT)^{3/2}_{2980}$, in which D is the dielectric constant of water at the absolute temperature, T, and primed quantities refer to the temperature for which corrections are to be calculated. From the values for

$-\log f'$ so obtained the corrections to be applied to various magnitudes of f were computed and plotted for convenient interpolation. This correction takes account of the temperature-variable factor in the "A" of the Debye-Hückel limiting law, but not of the less influential $(DT)^{1/2}$ term in the denominator of the more complete Debye-Hückel approximation, i.e., the "b" of equation (24).

Except at the lowest and highest temperatures (0°C. and 60°C.) the ionization constants obtained are self-consistent and almost independent of concentration. The stoichiometrical activity coefficients reported by Harned and Hamer for the very dilute solutions at 0°C. lead to widely inconsistent values of K for which no extrapolation is possible. The results at 60° are irregular enough to make extrapolation uncertain. The values of the constant obtained by extrapolation are as follows:

Temperature	15°C.	25°C.	40°C.	60°C.
$K_{\text{HSO}_4^-}$	.0180	.0127	.0084	(.0058)

The plot of $R \log K$ vs $1/T$ is almost linear between 15° and 40°C. , and has a slope leading to an average value of ΔH° of -5300 calories in this range.

Still another estimate of the heat of ionization of the bisulfate ion may be made from the experiments upon the heat of dilution of sulfuric acid that have been made by a number of workers.¹ The actual dilution data are in substantial agreement in the ranges in which the concentrations studied overlap, but there have been different choices of a method of extrapolation to infinite dilution, with resulting conflicts in the values adopted for the integral heat of dilution of sulfuric acid. We may avoid the uncertainties from extrapolation by basing our calculations upon the heat of dilution from one experimentally accessible concentration to another. The experiments of Lange, Monheim and Robinson at concentrations of from .05 m. to .00005 m. (to which Debye-Hückel theory for the heat of dilution of strong electrolytes might be expected to apply if ionization were complete), are best suited for the calculation. We make the following assumptions:

¹Brønsted, *Z. Physik. Chem.*, **68**, 693 (1910); Groenier, Ph. D. Thesis, The University of Chicago, 1931; Lange, Monheim and Robinson, *J.A.C.S.*, **55**, 4733 (1933).

(1) The heat effect due to the further separation of existing ions as a solution of sulfuric acid is diluted is of the same magnitude as the total heat effect for the similar dilution of a mixture of two strong electrolytes such as sodium chloride and sodium sulfate; the major part of the observed heat of dilution of sulfuric acid is thus attributed to the effects accompanying the further ionization of bisulfate ion. The heat of ionization at infinite dilution of the amount of HSO_4^- present at the beginning of the dilution may then be approximated by the subtraction of the estimated "normal" integral heats of dilution of the uni-univalent electrolyte, $\text{H}^+(\text{HSO}_4^-)$, and of the completely ionized H_2SO_4 present in a given solution from the observed integral heat of dilution.

(2) The amount of HSO_4^- ionized during the same dilution process (i.e., to infinite dilution) may be calculated from the ionization constant of HSO_4^- and the activity coefficients of H^+ , SO_4^{2-} and HSO_4^- ions, as estimated from the Debye-Hückel expression.

The steps in the calculation were as follows:

(a) The fraction of HSO_4^- ionized at each concentration of sulfuric acid considered was read from a curve representing the equation,

$$(\text{SO}_4^{2-}) = K_{\text{HSO}_4^-} \frac{(\text{HSO}_4^-)}{(\text{H}^+)} \frac{f_{\text{HSO}_4^-}}{f_{\text{SO}_4^{2-}} \cdot f_{\text{H}^+}} \quad (7)$$

(b) We define:

α_1 = fraction of HSO_4^- dissociated in solution of molality m_1 .

$Q_{(m)}$ = Heat absorbed when the amount of HSO_4^- present in a solution containing one mol of H_2SO_4 of the gross concentration, m , is ionized at infinite dilution.

ϕ_{H_∞} = integral heat of dilution to infinitely dilute solution, per mol of solute, i.e., the relative apparent molal heat content.

$\Delta H_{m_1-m_2} = \phi_{H_\infty}(\text{H}_2\text{SO}_4 \text{ at } m_1) - \phi_{H_\infty}(\text{H}_2\text{SO}_4 \text{ at } m_2)$. This is the quantity given directly by each dilution experiment of Lange, Monheim and Robinson.

The heat absorbed by the ionization of the residual bisulfate ion in the amount of m molal solution containing one mol of H_2SO_4 was estimated by the equation,

$$Q_{(m)} = \phi_{H\infty} H_2SO_4 - [\phi_{H\infty} NaCl \times (1 - \alpha)] - [\phi_{H\infty} Na_2SO_4 \times \alpha] \quad (8)^1$$

where $\phi_{H\infty} NaCl$ and $\phi_{H\infty} Na_2SO_4$ were taken for solutions of the same ionic strength as that of the sulfuric acid, corrected for the partial ionization of the bisulfate ion.

Two sets of highly ionized electrolytes were employed for alternative estimates of the "normal" integral heat of dilution to infinity of the fully ionized H_2SO_4 and of the $H^+ + HSO_4^-$ present at each concentration. In one case Na_2SO_4 and $NaCl$ were chosen as comparable strong electrolytes for which precise dilution data were available. For an alternative calculation HCl was taken as the 1-1 electrolyte and Li_2SO_4 , whose heat of dilution exceeds that of Na_2SO_4 in about the same proportion that that of HCl exceeds the heat of dilution of $NaCl$, was selected for the 2-1 type. The results of both methods of computation appear in Table 1.

(c) The heat of ionization, ΔH^0 , per mol. of HSO_4^- dissociated in the experimental dilution was calculated as

$$\Delta H^0 = \frac{Q_{(m_1)} - Q_{(m_2)}}{(1 - \alpha_1) - (1 - \alpha_2)} \quad (9)$$

in which

$$Q_{m_1} - Q_{m_2} = \Delta H_{m_1-m_2} - \phi_{H\infty}(NaCl, \mu_1) \cdot (1 - \alpha_1) - \phi_{H\infty}(Na_2SO_4, \mu_1) \cdot \alpha_1 + \phi_{H\infty}(NaCl, \mu_2) \cdot (1 - \alpha_2) + \phi_{H\infty}(Na_2SO_4, \mu_2) \cdot \alpha_2$$

It will be observed that the next to the last ΔH^0 in each series is seriously inconsistent. This value corresponds to measurements in the most dilute solutions used by Lange, Monheim and Robinson and is subject to the largest experimental uncertainty in the series. This value and the following one, which by the dilution method employed is dependent upon it, have been excluded

¹Buck, Ph. D. Thesis, The University of Chicago (1935); MacDonald, Ph. D. Thesis, The University of Chicago (1936). The slope data of these workers were extrapolated to the Debye-Hückel value at zero ionic strength and the integral heats of dilution computed by graphical integration; Lange and Streeck, Z. Physik Chem. A 157, 1 (1931); Young and Seligmann, J.A.C.S., 60, 2379 (1938).

from the averages taken. From these calculations we find ΔH° for the ionization of HSO_4^- to be -5300 ± 100 calories. In the computations tabulated below the fraction of HSO_4^- ionized at each dilution was computed from $K = .01015$, as reported in the experimental part of this paper. A preliminary calculation, made with the assumption that $K = .0120$ (Hamer), gave values for ΔH° about 200 calories larger than those shown.

TABLE 1 - ΔH° FROM HEATS OF DILUTION OF SULFURIC ACID

Initial Molality m_1	Final Molality m_2	ΔH m_1 to m_2	Net Corr. for Normal Dilution	$Q_{m_1} - Q_{m_2}$	Mols HSO_4 Ionized per mol of Acid Diluted	ΔH° cal/mol
Dilution Corrections Based Upon Na_2SO_4 and NaCl						
.05022	.000734	-3410	67	-3343	.621	-5382
.05022	.001458	-3048	52	-2996	.554	-5408
.05022	.002170	-2770	42	-2728	.504	-5412
.02509	.0003672	-3086	75	-3011	.563	-5348
.02509	.0007290	-2836	64	-2772	.520	-5331
.01256	.0001836	-2623	80	-2543	.477	-5330
.01256	.0003646	-2452	69	-2382	.450	-5295
.00627	.0000918	-2055	76	-1979	.370	-5349
.00627	.0001822	-1936	69	-1867	.356	-5244
.003134	.0000459	-1711	71	-1640	.264	-(6212)
.003134	.0000911	-1517	64	-1453	.256	-(5675)
Average ΔH° (excluding last two values)						-5344
Dilution Corrections Based Upon Li_2SO_4 and HCl						
.05022	.000734	-3410	116	-3294	.621	-5303
.05022	.001458	-3048	100	-2948	.554	-5321
.05022	.002170	-2770	89	-2681	.504	-5319
.02509	.0003672	-3086	110	-2976	.563	-5285
.02509	.0007290	-2836	95	-2741	.520	-5271
.01256	.0001836	-2623	102	-2521	.477	-5284
.01256	.0003646	-2452	91	-2361	.450	-5246
.00627	.0000918	-2052	91	-1964	.370	-5308
.00627	.0001822	-1936	84	-1852	.356	-5202
.003134	.0000459	-1711	79	-1632	.264	-(6182)
.003134	.0000911	-1517	72	-1445	.256	-(5644)
Average ΔH° (excluding last two values)						-5282

Lange, Monheim and Robinson, on the basis of a linear extrapolation of their data to zero concentration, give ϕ_{H_∞} for H_2SO_4 as -330 calories at their most dilute experimental concentration, .0001 molal. In such a solution the HSO_4^- ion is 98.2%

ionized; the correction for simple dilution of the solute species present amounts to 23 calories per mol of H_2SO_4 diluted. We therefore calculate ΔH° for the ionization of HSO_4^- to be -17,000 calories. The inconsistency of this result with those obtained above indicates clearly the unsatisfactory nature of Lange, Monheim and Robinson's linear extrapolation of their data for sulfuric acid.

Boyd¹ recently made a number of measurements in this laboratory of the heat effect on mixing dilute solutions of hydrochloric acid and sodium sulfate. Among these experiments were two which resulted in solutions whose ionic strengths were low enough to encourage an attempt to calculate the concentration of HSO_4^- present, and from this and the measured heat effect to estimate the heat of ionization per mol of bisulfate ion. The calculation is presented in Table 2. The concentration of HSO_4^- was found from the relation,

$$(\text{HSO}_4^-) = \frac{[m_{\text{HCl}} - (\text{HSO}_4^-)][(m_{\text{Na}_2\text{SO}_4} - (\text{HSO}_4^-))] f_{\text{H}^+} f_{\text{SO}_4^{2-}}}{.01015 \cdot \frac{f_{\text{HSO}_4^-}}{f_{\text{HSO}_4^-}}} \quad (10)$$

which is readily solved by the method of successive approximations. K was taken as .01015, from the experimental part of this thesis, and Kielland's table of activity coefficients was again employed.

Aside from the actual heat absorbed during the formation of bisulfate ion, the most important heat effect during mixing would seem to be that attendant upon the dilution of the relatively concentrated HCl solution to an ionic strength about one-fourth as great. This will result in an evolution of heat of the order of 100 calories per mol of HCl diluted.

ΔH° may be obtained from ΔH_m , the heat of reaction at the final ionic strength resulting from mixing, by the relation

$$\Delta H^\circ = \Delta H_m + \int_{\infty}^{\infty} \text{NaCl} + \int_{\infty}^{\infty} \text{NaHSO}_4 - \int_{\infty}^{\infty} \text{HCl} - \int_{\infty}^{\infty} \text{Na}_2\text{SO}_4 \quad (11)$$

in which $\int_{\infty}^{\infty}$ signifies the integral heat of dilution per mol of the solute specified from the final ionic strength of the experiment to infinite dilution. The heat of dilution of HCl was taken from the curve constructed for the preceding calculation upon

¹Boyd, unpublished work.

heats of dilution of H_2SO_4 . For NaCl the data of Young and Vogel¹ were used, and for Na_2SO_4 those of Lange and Streeck.² The approximate nature of the whole calculation made it unnecessary to recalculate these heats of dilution by the more precise methods developed in this laboratory by Young and his co-workers.³

Adequate experimental basis does not at present exist to justify the assumption, implied above, that in a mixture of electrolytes the heat of dilution of each constituent is a function only of the total ionic strength of the solution. For dilute solutions, however, it seems a reasonable first approximation. A still rougher approximation is involved in the assumption that the experimentally inaccessible heat of dilution of $\text{Na}(\text{HSO}_4^-)$ is equal to that of NaCl at similar concentrations.

TABLE 2 - CALCULATION OF ΔH° FROM HEATS OF MIXING HCl AND Na_2SO_4

	Experiment 6	Experiment 7
Initial molality of Na_2SO_4	.05485	.02743
Grams of Na_2SO_4 solution taken	778.47	777.27
Initial molality of HCl	.58969	.29345
Grams of HCl solution taken	71.775	71.559
Total weight of water taken	843.36	845.88
Final molality of Na_2SO_4	.05028	.02513
Final molality of HCl	.04916	.02459
Computed molality of HSO_4^-	.02305	.00945
Computed amount of HSO_4^- formed (mols)	.01945	.00800
μ in final solution	.3924	.2848
Correction for dilution of HCl during mixing, cal/per mol	-140.	-95.
Mols HCl diluted	.0348	.0208
Correction for dilution of HCl used, calories	-4.87	-1.98
Measured heat absorbed, calories	89.06	35.67
Corrected heat absorbed by formation of HSO_4^-	93.93	37.65
ΔH_m for ionization of HSO_4^-	-4830.	-4710.
Correction for dilution to ∞	-230.	-210.
ΔH° , for ionization of HSO_4^-	-5060.	-4920.

¹Young and Vogel, J.A.C.S., 54, 3030 (1932).

²Lange and Streeck, loc. cit.

³Young and Groenier, J.A.C.S., 58, 187 (1936); Young and Seligmann, loc. cit.

An error of 6% in the value of K would produce an error of approximately 3% in the calculated value of ΔH° . Similarly a 2% error in the magnitude assigned to $f_{H^+} \cdot f_{SO_4}/f_{HSO_4^-}$ for the solution considered would result in about a 1% error in ΔH° .

The values of ΔH° for the ionization of HSO_4^- at $25^\circ C$. indicated by previous work may be summarized as follows:

Source	ΔH°
Jones and Douglas, 1901	not detectable
Luther, 1907	not detectable
Noyes and Eastman, 1907	-5,400. cal.
Noyes and Eastman, from Thomsen's data (-5,020 at $18^\circ C$.)	-5,370.
Muller, 1913	-4,200.
Hamer, 1934	-2,229.
Pitzer, 1937	-5,200.
Recalculation of Noyes and Eastman's data for 25° and 18° by the method of Sherrill and Noyes	-5,800.
Calculated from Harned and Hamer's activity coefficients for H_2SO_4	-5,300.
Calculated from heat of dilution data of Lange, Monheim, and Robinson	-5,300.
Calculated from Boyd's heat of mixing experiments	-4,990.

EXPERIMENTAL PART

The evidence from the very different sources just summarized casts serious doubt upon the accuracy of Hamer's widely cited ionization constants of bisulfate ion from 0° to $60^\circ C$. from which his value of 2229 calories for ΔH° of ionization at 25° is derived. Some different method was therefore sought for the determination of $K_{HSO_4^-}$ over the temperature range studied by Hamer. The selection of a method should be based upon the following considerations.

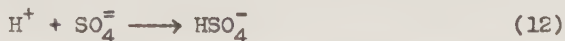
(1) Since it is desired to resolve a conflict in the ΔH 's derived from calorimetric and from e. m. f. measurements, neither of these techniques should be employed.

(2) An acid with an ionization constant of the order of 10^{-2} is so nearly completely ionized in solutions more dilute than .001 molar that very slight experimental errors lead to large percentage errors in the value of the small amount of undissociated acid present; these errors affect the calculated K proportionately. If the slight errors are systematic, a large

but unsuspected error in the extrapolation to K at infinite dilution may result. The situation differs from that for a weaker acid like acetic, for which the ratio of the ionized to the unionized portion becomes more favorable as we pass to more dilute solutions, and thus compensates in part for the increased experimental difficulties. The method chosen for the bisulfate ion, then, should depend upon measurements made with solutions whose concentrations are above .001 and below .15 molal. This upper limit is small enough so that the effect of the ionic strength of the solutions on the activities of the ions may be estimated within one or two per cent by some empirical extension of the Debye-Hückel theory.¹

(3) The concentration of HSO_4^- ion in the solution should be obtained either directly or by measurements of changes in a quantity of comparable magnitude, rather than calculated from changes in the measured magnitude of much larger quantities, such as the total H^+ in sulfuric acid solutions. This dependence upon small differences in (relatively) much larger quantities is a major weakness of conductance methods, and of e. m. f. methods with electrodes reversible to hydrogen and to sulfate ion.

The method selected was based on measurements made by Mullane² during an investigation of the neutral salt effect on indicators in very dilute unbuffered solutions. He found that the color changes produced by the addition of sodium or potassium sulfate to the indicator solution were much larger than the consistently uniform effects exhibited by such salts as sodium or potassium chlorides, bromides and nitrates. An examination of Mullane's data showed that an approximately correct value of the ionization constant of the bisulfate ion could be derived from them if it was assumed that in the case of the alkali sulfates all of the deviation from the normal neutral salt effect could be attributed to a change in hydrogen ion concentration caused by the reaction,



A complete account of the experimental procedures adopted, and of the design of a photoelectric spectrophotometer capable of

¹Naidich and Ricci, J.A.C.S., 61, 3268 (1939).

²J. Mullane, Ph. D. Thesis, The University of Chicago.

measuring changes in pH to .001 unit, together with a discussion of a method by which the ionization constant of a weak acid may be calculated from the measurements, is given elsewhere by Klotz.¹ The essential features of the procedure were as follows.

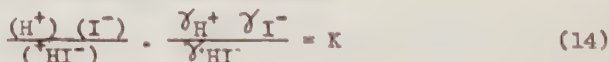
(1) Successive portions of the pure salt to be studied were added to the indicator solution in an absorption cell of 200 cm³ capacity. The relative light absorption of each solution so obtained was measured by comparison with a sample of the stock indicator solution in a cell of similar optical characteristics in a series of from five to nine alternate readings with the photoelectric spectrophotometer. The indicator solutions used in this study contained approximately 4×10^{-6} mols of methyl orange and 3 to 6×10^{-4} mols of hydrochloric acid per liter. All of the observations were made with light of about 5200 Å units. At each temperature separate series of measurements were made of the effects of NaCl, BaCl₂, and Na₂SO₄ upon the relative absorption of this light by the indicator solution. At 25° similar measurements were also made with KCl, K₂SO₄, KNO₃, and NaNO₃.

(2) From the ratios, $\left(\frac{I_r}{I}\right)$, of the light intensities transmitted by the reference cell and by the working cell respectively, the ratio,

$$R = \frac{I^-}{HI^-} = \frac{\log \left(\frac{I_r}{I}\right)_x - \log \left(\frac{I_r}{I}\right)_a}{\log \left(\frac{I_r}{I}\right)_x - \log \left(\frac{I_r}{I}\right)_b} \quad (13)$$

was calculated. The subscripts, x, a, and b denote respectively the absorption ratio for the salt solution, for the solution containing all of the indicator in the acid form, and for that containing all of it in the base form. Equation (13) takes account of the fact that the indicator absorbs light in its basic as well as its acid form.

The method of determining the change in hydrogen-ion concentration produced by the addition of sodium sulfate to the stock solution of methyl orange and HCl may be understood from a consideration of the indicator equilibrium,



which may be rewritten,

¹Klotz, Ph. D. Thesis, The University of Chicago, 1940.

$$-\log (H^+) = -\log K + \log R + \log f \quad (15)$$

where $f = \gamma_{H^+} \gamma_{I^-} / \gamma_{HI^-}$, and $R = \frac{(I^-)}{(HI^-)}$. If now we denote the magnitude of each of these quantities in a reference solution, such as the stock indicator solution, by the subscript o, we write

$$-\log (H^+)_o = -\log K + \log R_o + \log f_o \quad (16)$$

Subtracting 15 from 16 we obtain,

$$\log [(H^+)/ (H^+)_o] + \log f/f_o = \log R_o - \log R \quad (17)$$

We assume that when a neutral salt is added there is no change in (H^+) , but that the ratio, $R = (I^-)/(HI^-)$, is altered because of the changed activity coefficients of the ions involved in the equilibrium, i.e.

$$\text{for addition of a neutral salt} \left\{ \begin{array}{l} \log [(H^+)/ (H^+)_o] = 0 \\ \text{and} \end{array} \right. \quad (18)$$

$$\log f/f_o = \log R_o - \log R \quad (19)$$

For the addition of the salt of a "weak" acid, such as HSO_4^- , equation 17 (if we indicate quantities referring to the sulfate solution by a prime) becomes

$$\log [(H^+)'/ (H^+)_o] = \log R_o - \log R' - \log f'/f_o \quad (20)$$

For solutions of the same ionic strength, $f'/f_o = f/f_o$; so, from equations 19 and 20, we write

$$\text{Log} [(H^+)'/ (H^+)_o] = \text{Log} R - \log R' = \log S \quad (21)$$

The use of this equation implies the assumption that at a given ionic strength the effect of the electrolyte upon the activity coefficients of each ionic species involved in the indicator equilibrium is a function only of the ionic strength.

(3) To calculate for the bisulfate equilibrium the apparent or classical constant which employs molalities in place of activities we define the molalities of the ions concerned as shown below.

$$(H^+) = (H^+)_o S$$

$$(HSO_4^-) = (H^+)_o (1 - S)$$

$$(SO_4^{--}) = m - (HSO_4^-) = m - (H^+)_o (1 - S)$$

(m = molality of sodium sulfate.)

Then

$$K'' = \frac{(H^+) (SO_4^{2-})}{(HSO_4^-)} = \frac{(H^+)_0 S [m - (H^+)_0 (1 - S)]}{(H^+)_0 (1 - S)} \quad (22)$$

$$K'' = \frac{S [m - (H^+)_0 (1 - S)]}{(1 - S)}$$

It will be noted that this equation depends upon the actual value of $(H^+)_0$ (determined with a precision of .02 pH units for each lot of stock solution with a glass electrode) only to the extent of a small correction term for the concentration of the sulfate ion. Test calculations show that the error in K will not in the most unfavorable case exceed .3% for an error of 0.1 unit in the pH of the stock solution.

(4) The thermodynamic ionization constant, K' , was then calculated by the relation;

$$K' = K'' \frac{f_{H^+} f_{SO_4^{2-}}}{f_{HSO_4^-}} \quad (23)$$

Since the limiting-law expression for $-\log f$ is not applicable over the range of concentrations studied, the more complete form of the Debye-Hückel expression,

$$-\log f = \frac{4 A \sqrt{\mu}}{1 - b \sqrt{\mu}} \quad (24)$$

in which $b = 50.3 a_1 / (DT)^{1/2}$ was employed. The values of the constant "b" were selected empirically so that the resulting values of K' at various concentrations permitted a linear and approximately horizontal extrapolation to the value, K, at zero ionic strength. Variations of 10% in the "b" chosen changed the slope of the extrapolation, but did not appreciably affect the linearity or the value indicated at zero ionic strength. A perfect choice for the magnitude of "b" would have permitted a simple averaging of the values of the equilibrium constant at finite concentrations, but the observed constancy of the extrapolation obtained with somewhat different values of "b" simplified the calculations considerably. The extrapolations upon which the reported values of K are based are shown graphically in Figure 1. The formulae used for $-\log f$ in the extrapolations at the various temperatures appear in Table 3.

If the factors affecting the a_1 term in the above form of the Debye-Hückel equation do not vary with the temperature, the

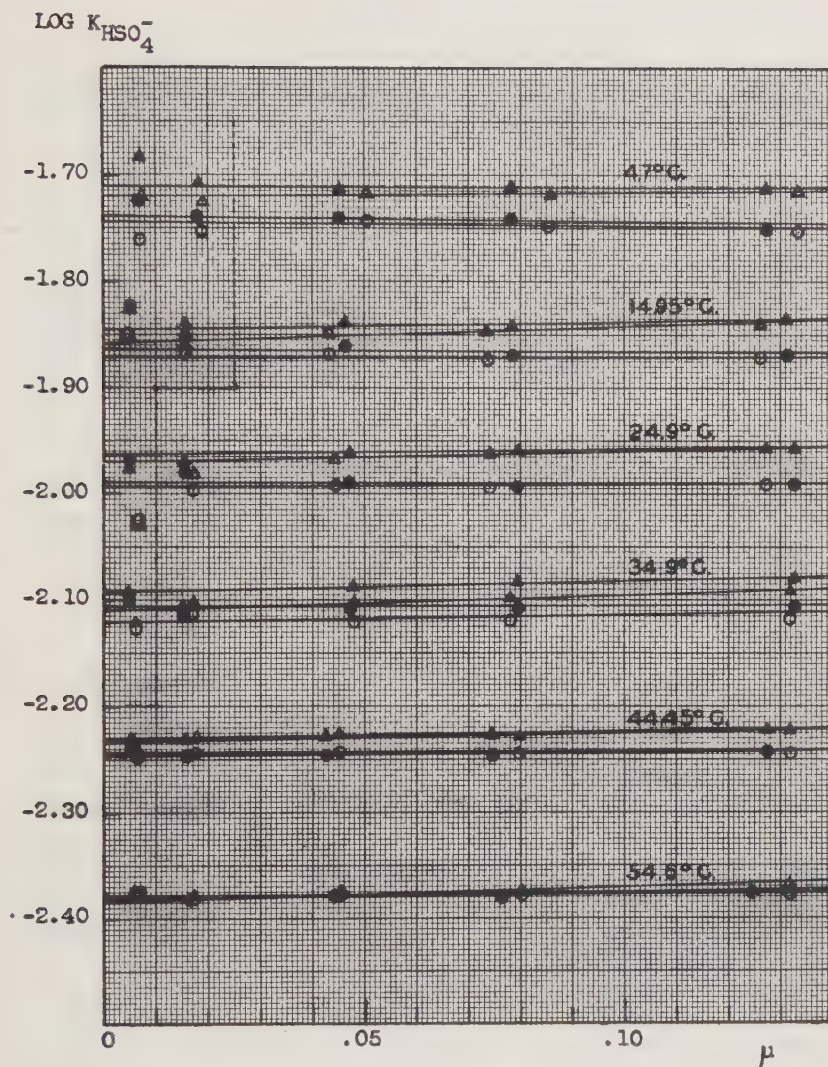


Fig. 1.--Extrapolations for $\text{Log } K$ of HSO_4^- at $m = 0$

△ △ BaCl_2 as reference salt.

○ ● NaCl as reference salt.

For points to the left of the broken line, K would change 5 per cent for an error of .002 in $\log R_0/R$.

TABLE 3 - CONSTANTS FOR DEBYE-HÜCKEL EXPRESSION

Temperature	-log f with NaCl Reference Salt	-log f with BaCl ₂ Reference Salt
4.7°C.	$(1.968 \sqrt{\mu}) / (1 - 2.0 \sqrt{\mu})$	$(1.968 \sqrt{\mu}) / (1 - 1.9 \sqrt{\mu})$
14.95°	$(2.000 \sqrt{\mu}) / (1 - 2.0 \sqrt{\mu})$	$(2.000 \sqrt{\mu}) / (1 - 1.9 \sqrt{\mu})$
24.9°	$(2.034 \sqrt{\mu}) / (1 - 1.9 \sqrt{\mu})$	$(2.034 \sqrt{\mu}) / (1 - 1.85 \sqrt{\mu})$
34.9°	$(2.070 \sqrt{\mu}) / (1 - 2.0 \sqrt{\mu})$	$(2.070 \sqrt{\mu}) / (1 - 1.9 \sqrt{\mu})$
44.45°	$(2.106 \sqrt{\mu}) / (1 - 1.9 \sqrt{\mu})$	$(2.106 \sqrt{\mu}) / (1 - 1.80 \sqrt{\mu})$
54.6°	$(2.147 \sqrt{\mu}) / (1 - 1.9 \sqrt{\mu})$	$(2.147 \sqrt{\mu}) / (1 - 1.9 \sqrt{\mu})$

coefficient, b, of $\sqrt{\mu}$ in the denominator of these expressions should increase by 3.3% as we go from 5° to 55°C. The corresponding change in -log f for the most concentrated solutions studied would be 1.25%. The data obtained are not precise enough to demonstrate a change of this magnitude.

DISCUSSION OF ERRORS

Klotz¹ has discussed the sources of error in the measurement of ionization constants by this method. He concludes that uncertainties arising from volume changes accompanying the addition of the solid salts, from changes in hydrogen ion concentration due to shifts in indicator equilibrium as salts are added, from dissolved CO₂, or from failure of Beer's law, are too small to interfere with a precision of one per cent in the K's determined. Two larger sources of error remain.

One source of error results from the very considerable temperature coefficient of the indicator constant for methyl orange. If the temperatures of the two cells should vary with respect to each other during a series of measurements serious errors in the observed $\left(\frac{I_r}{I}\right)$ readings would follow. The consistency of the experimental results obtained by two observers over a period of several months indicates that random errors from this source are small. It still remains possible that small systematic

¹Loc. cit.

errors arise from this source when measurements are made 20° or more away from room temperature. Such errors might be opposite in sign at high and at low temperatures, and on that account might affect the heats of ionization calculated from the ionization constants. The general consistency of the neutral salt curves for sodium chloride at different temperatures indicates that such systematic effects are small.

The second and largest source of uncertainty affecting the values of the K 's reported is that there are specific salt effects upon the indicator equilibrium at the lowest concentrations for which reliable values of K can be calculated. We have so far no way of determining which neutral salt most nearly duplicates the effect of sulfate ions (and of the minute amounts of hydrogen and of bisulfate ions present) upon the methyl orange equilibrium. Experiments at 25°C . reported by Klotz¹ showed that the use of NaCl , BaCl_2 , and KCl as reference neutral salts for the calculation of K from experiments made with Na_2SO_4 led to different values of K . The K from BaCl_2 , with its doubly charged positive ion, exceeded that obtained with NaCl by six per cent, while the constant from KCl was only 3.5 per cent larger than that from NaCl .

On the other hand, K 's calculated from the salt pairs Na_2SO_4 - NaCl , Na_2SO_4 - NaNO_3 , and K_2SO_4 - KCl agree within the experimental uncertainty of about one per cent; this suggests that specific effects on the indicator equilibrium may be less pronounced from negative than from positive ions. It is still possible that the sulfate ion, with its double negative charge, may have an effect on the indicator equilibrium different from that of the anions of uni-univalent neutral salts. However, we would expect for theoretical reasons that the large negative indicator ion would be more susceptible than the hydrogen or the zwitter ion to specific salt effects, so that the change from chloride ion to sulfate ion should produce less uncertainty in K than the change from sodium to barium ion described above. At present we conclude that while the error in the K 's calculated from Na_2SO_4 - NaCl is probably less than two per cent, it is not impossible that the values of K tabulated for 25°C . and below are in error by as much as six per cent. The uncertainty should become less

¹Ibid.

as we go to higher temperatures. Such a systematic error in K need not introduce a correspondingly large error in ΔH° , which depends only upon the differences in K at different temperatures. ΔH° would be affected only 3% by a uniform trend from a correct K at one end of the temperature range to one in error by 6% at the other end. The heats of ionization calculated from the two series of constants agree within one hundred calories at 25°C .; they show their largest difference, 464 calories, at 55°C .

The uncertainty resulting from specific salt effects is large enough, when compared with the precision of the experimental procedure, that we may reasonably hope that the reliability of the constants can be improved by measurements with some other indicator which shows smaller specific salt effects than methyl orange. Methyl orange was chosen for this work because of its stability, and because its behavior in neutral salt solutions had already been investigated by several workers.

RESULTS

The ionization constant of the bisulfate ion was determined at intervals of approximately 10° from 5° to 55°C .; both barium chloride and sodium chloride were used as standards to correct for the neutral salt effect. At each temperature, two series of measurements of the effect of sodium sulfate on the relative light absorption of the indicator solution were made by different observers. The data obtained are collected in Table 4, and presented graphically in Figures 2 and 3. In Figure 2, $\log \left(\frac{I^+}{I^-} \right)_0 - \log \left(\frac{I^+}{I^-} \right)$ for the sodium sulfate series is plotted against the square root of the ionic strength. The quantities plotted have been corrected by extrapolation so that $\log \left(\frac{I^+}{I^-} \right)_0$ refers to a common ionic strength, $\mu^{1/2} = .0150$, for all of the measurements. (The quantity to be added to $\log \left(\frac{I^+}{I^-} \right)_0 - \log \left(\frac{I^+}{I^-} \right)$ for a particular series was obtained by graphical extrapolation of the neutral salt curve through the original reference point to $\mu^{1/2} = .0150$. The corresponding increment in $\log \left(\frac{I^+}{I^-} \right)_0 - \log \left(\frac{I^+}{I^-} \right)$ was the appropriate correction.) The corresponding values for the measurements with sodium chloride at 5°C . and 55°C . appear for purposes of comparison. These, and the data for barium chloride, are presented on a larger scale in Figure 3.

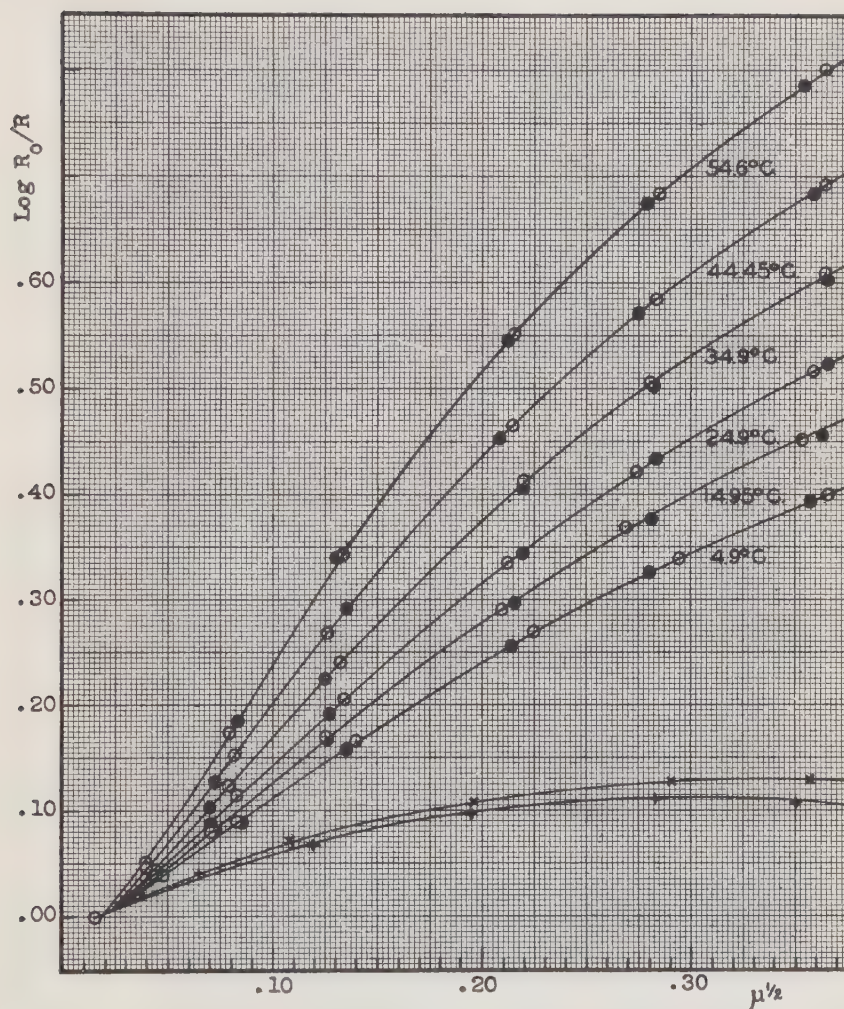


Fig. 2.-- $\text{Log } R_0/R$ for Sodium Sulfate and Sodium Chloride with Methyl Orange.

- o • Sodium sulfate (Two observers).
- x Sodium chloride at 54.6°C.
- + Sodium chloride at 4.9°C.

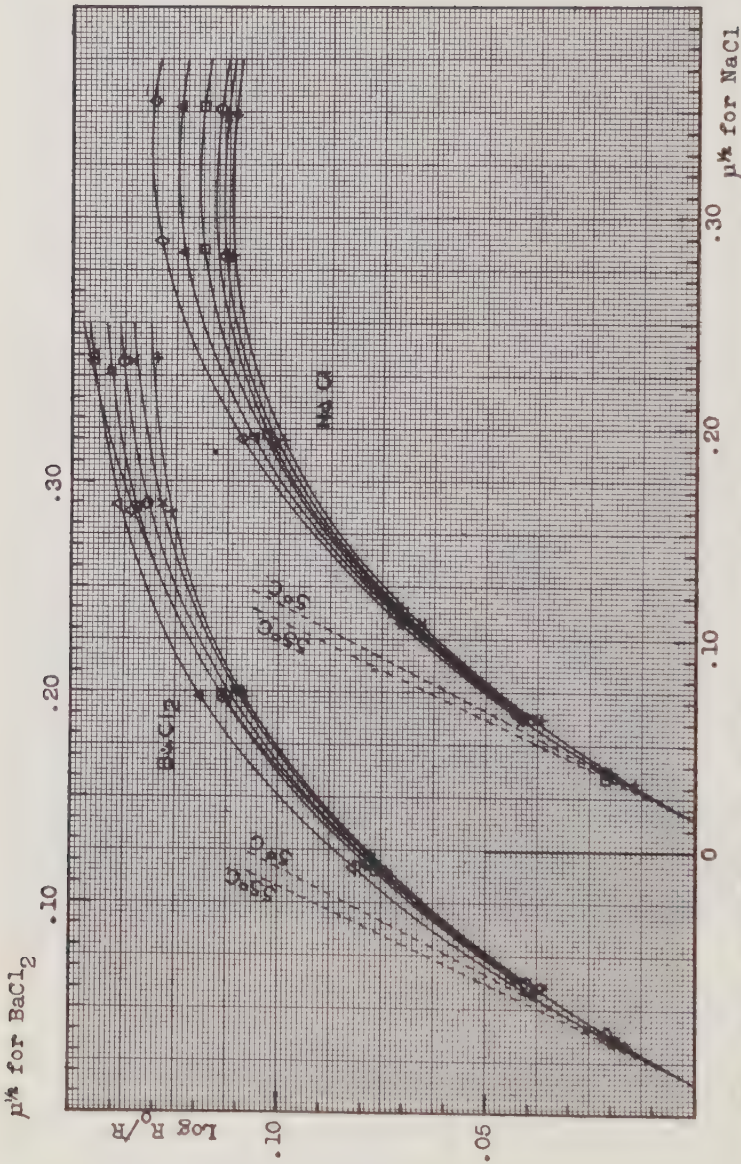


Fig. 3.-- $\text{Log } R_0/R$ for Barium Chloride and for Sodium Chloride with Methyl Orange
 Key to symbols: + = 4.7° C.; x = 14.95° C.; o = 24.9° C.; □ = 34.9° C.; Δ = 44.45° C.; ◇ = 54.6° C.
 ----- Debye-Hückel limiting law slopes.

TABLE 4 - SALT EFFECTS ON METHYL ORANGE

Solution Observed	Molality of Salt	$\mu^{1/2}$	Log (I/I _r)	Log (R _o /R)	Log R _o /R Ref. Point $\mu^{1/2} = .0150$
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NaCl at 4.7°C.

Acid form			[-.3325]		
Base form			+.5623		
Stock solution		.0187	+.0100	[.0000]	-.0035
Salt addition(1)	.00064	.0315	.0154	-.0111	-.0146
" " (2)	.00354	.0624	.0265	-.0337	-.0372
" " (3)	.01215	.1118	.0425	-.0658	-.0696
" " (4)	.03749	.1945	.0576	-.0957	-.0993
" " (5)	.08003	.2825	.0641	-.1085	-.1120
" " (6)	.12202	.3498	.0632	-.1067	-.1104

BaCl₂ at 4.7°C.

Acid form			[-.3600]		
Base form			+.5348		
Stock solution		.0187	-.0105	[.0000]	-.0035
Salt addition(1)	.00026	.0336	-.0037	-.0139	-.0174
" " (2)	.00105	.0592	+.0069	-.0352	-.0387
" " (3)	.00490	.1227	.0266	-.0745	-.0780
" " (4)	.01293	.1978	.0422	-.1052	-.01087
" " (5)	.02703	.2854	.0514	-.1232	-.1267
" " (6)	.04246	.3574	.0530	-.1263	-.1298

Na₂SO₄ at 4.7°C.

Acid form			[-.3623]		
Base form			+.5325		
Stock solution		.0187	+.0125	[.0000]	-.0035
Salt addition(1)	.00062	.0467	.0053	-.0359	-.0392
" " (2)	.00219	.0832	.0304	-.0858	-.0892
" " (3)	.00638	.1396	.0698	-.1628	-.1664
" " (4)	.01685	.2255	.1232	-.2666	-.2701
" " (5)	.02853	.2931	.1587	-.3368	-.3403
" " (6)	.04447	.3657	.1890	-.3980	-.4015

Na₂SO₄ at 4.7°C.

Acid form			[-.3624]		
Base form			+.5324		
Stock solution		.0187	-.0130	[.0000]	-.0035
Salt addition(1)	.00052	.0437	+.0017	-.0298	-.0333
" " (2)	.00229	.0850	.0296	-.0853	-.0888
" " (3)	.00594	.1348	.0647	-.1540	-.1575
" " (4)	.01509	.2136	.1154	-.2523	-.2558
" " (5)	.02609	.2803	.1508	-.3219	-.3254
" " (6)	.04247	.3574	.1849	-.3909	-.3944

TABLE 4 - Continued

Solution Observed	Molality of Salt	$\mu^{1/2}$	Log (I/I _r)	Log (R ₀ /R)	Log R ₀ /R Ref. Point $\mu^{1/2} = .0150$
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NaCl at 15.1°C.

Acid form			[-.2159]		
Base form			+.3317		
Stock solution		.0235	+.0058	[.0000]	-.0078
Salt addition(1)	.00065	.0346	.0095	-.0122	-.0200
" " (2)	.00327	.0618	.0163	-.0344	-.0422
" " (3)	.01112	.1080	.0235	-.0582	-.0660
" " (4)	.03646	.1924	.0347	-.0936	-.1014
" " (5)	.07880	.2817	.0383	-.1050	-.1128
" " (6)	.12103	.3487	.0384	-.1054	-.1132

BaCl₂ at 14.9°C.

Acid form			[-.2159]		
Base form			+.3317		
Stock solution		.0235	+.0050	[.0000]	-.0078
Salt addition(1)	.00038	.0411	+.0105	-.0180	-.0258
" " (2)	.00118	.0640	.0159	-.0357	-.0435
" " (3)	.00444	.1178	.0269	-.0715	-.0793
" " (4)	.01317	.2002	.0369	-.1032	-.1110
" " (5)	.02766	.2890	.0424	-.1207	-.1285
" " (6)	.04221	.3567	.0447	-.1280	-.1358

Na₂SO₄ at 15.0°C.

Acid form			[-.2159]		
Base form			+.3317		
Stock solution		.0235	+.0073	[.0000]	-.0078
Salt addition(1)	.00024	.0356	.0124	-.0168	-.0245
" " (2)	.00143	.0696	.0295	-.0720	-.0798
" " (3)	.00505	.1253	.0581	-.1629	-.1706
" " (4)	.01437	.2089	.0958	-.2834	-.2911
" " (5)	.02458	.2726	.1198	-.3622	-.3700
" " (6)	.04135	.3530	.1438	-.4444	-.4522

Na₂SO₄ at 14.9°C.

Acid form			[-.2163]		
Base form			+.3313		
Stock solution		.0235	+.0058	[.0000]	-.0078
Salt addition(1)	.00037	.0407	.0132	-.0247	-.0325
" " (2)	.00152	.0715	.0283	-.0731	-.0809
" " (3)	.00512	.1261	.0559	-.1609	-.1687
" " (4)	.01543	.2164	.0963	-.2899	-.2977
" " (5)	.02624	.2815	.1207	-.3702	-.3780
" " (6)	.04387	.3636	.1444	-.4514	-.4592

TABLE 4 - Continued

Solution Observed	Molality of Salt	$\mu^{1/2}$	Log (I/I _r)	Log (R ₀ /R)	Log R ₀ /R Ref. Point $\mu^{1/2} = .0150$
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NaCl at 24.9°C

Acid form			[-.2425]		
Base form			+.2870		
Stock solution		.0235	+.0074	[.0000]	-.0078
Salt addition(1)	.00076	.0362	.0112	-.0125	-.0203
" " (2)	.00353	.0639	.0175	-.0333	-.0411
" " (3)	.01186	.1114	.0268	-.0638	-.0716
" " (4)	.03684	.1934	.0361	-.0940	-.1018
" " (5)	.07974	.2824	.0394	-.1051	-.1129
" " (6)	.12319	.3517	.0398	-.1066	-.1144

BaCl₂ at 24.9°C.

Acid form			[-.2393]		
Base form			[+.2867]		
Stock solution		.0235	+.0066	[.0000]	-.0078
Salt addition(1)	.00032	.0389	.0105	-.0129	-.0207
" " (2)	.00112	.0625	.0166	-.0331	-.0409
" " (3)	.00442	.1175	.0276	-.0694	-.0772
" " (4)	.01320	.2004	.0376	-.1023	-.1101
" " (5)	.02774	.2894	.0443	-.1244	-.1322
" " (6)	.04231	.3571	.0459	-.1300	-.1378

Na₂SO₄ at 24.9°C.

Acid form			[-.2383]		
Base form			+.2877		
Stock solution		.0235	+.0079	[.0000]	-.0078
Salt addition(1)	.00045	.0436	.0174	-.0314	-.0392
" " (2)	.00208	.0824	.0408	-.1086	-.1164
" " (3)	.00578	.1338	.0679	-.1995	-.2073
" " (4)	.01480	.2120	.1047	-.3283	-.3361
" " (5)	.02479	.2737	.1276	-.4144	-.4222
" " (6)	.04260	.3583	.1510	-.5101	-.5179

Na₂SO₄ at 24.9°C.

Acid form			[-.2390]		
Base form			+.2870		
Stock solution		.0235	+.0069	[.0000]	-.0078
Salt addition(1)	.00039	.0415	.0157	-.0291	-.0369
" " (2)	.00150	.0711	.0313	-.0806	-.0884
" " (3)	.00516	.1266	.0623	-.1837	-.1915
" " (4)	.01583	.2192	.1064	-.3380	-.3458
" " (5)	.02660	.2835	.1296	-.4260	-.4338
" " (6)	.04438	.3657	.1517	-.5172	-.5250

TABLE 4 - Continued

Solution Observed	Molality of Salt	$\mu^{1/2}$	Log (I/I _r)	Log (R _o /R)	Log R _o /R Ref. Point $\mu^{1/2} = .0150$
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NaCl at 34.9°C.

Acid form			[-.3847]		
Base form			+.3140		
Stock solution		.0184	+.0039	[.0000]	-.0036
Salt addition(1)	.00083	.0342	.0139	-.0177	-.0213
" " (2)	.00353	.0622	.0208	-.0353	-.0389
" " (3)	.01229	.1123	.0338	-.0689	-.0725
" " (4)	.03845	.1970	.0457	-.0997	-.1033
" " (5)	.08103	.2853	.0513	-.1146	-.1182
" " (6)	.12411	.3528	.0513	-.1146	-.1182

BaCl₂ at 34.9°C.

Acid form			[-.3805]		
Base form			+.3180		
Stock solution		.0184	+.0111	[.0000]	-.0036
Salt addition(1)	.00028	.0346	.0168	-.0143	-.0179
" " (2)	.001034	.0587	.0254	-.0362	-.0398
" " (3)	.00431	.1152	.0396	-.0728	-.0764
" " (4)	.01299	.1983	.0540	-.1105	-.1141
" " (5)	.02741	.2874	.0619	-.1316	-.1352
" " (6)	.04124	.3522	.0641	-.1374	-.1410

Na₂SO₄ at 34.9°C.

Acid form			[-.3807]		
Base form			+.3180		
Stock solution		.0184	+.0095	[.0000]	-.0036
Salt addition(1)	.00037	.0381	.0229	-.0343	-.0421
" " (2)	.00195	.0787	.0567	-.1219	-.1255
" " (3)	.00567	.1317	.0982	-.2365	-.2401
" " (4)	.01598	.2197	.1535	-.4096	-.4132
" " (5)	.02613	.2806	.1792	-.5038	-.5074
" " (6)	.04401	.3638	.2037	-.6067	-.6103

Na₂SO₄ at 34.9°C.

Acid form			[-.3812]		
Base form			+.3175		
Stock solution		.0184	+.0090	[.0000]	-.0036
Salt addition(1)	.000354	.0374	.0215	-.0317	-.0353
" " (2)	.00152	.0700	.0476	-.0988	-.1024
" " (3)	.00509	.1249	.0929	-.2227	-.2263
" " (4)	.01595	.2195	.1508	-.4023	-.4059
" " (5)	.02653	.2833	.1776	-.4996	-.5032
" " (6)	.04436	.3553	.2017	-.6001	-.6037

TABLE 4 - Continued

Solution Observed	Molality of Salt	$\mu^{1/2}$	Log (I/I _r)	Log (R ₀ /R)	Log R ₀ /R Ref. Point $\mu^{1/2} = .0150$
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NaCl at 44.4°C.

Acid form			[-.4010]		
Base form			+.2757		
Stock solution		.0185	+.0104	[.0000]	-.0036
Salt addition(1)	.00083	.0342	.0161	-.0157	-.0193
" " (2)	.00372	.0637	.0248	-.0394	-.0430
" " (3)	.01226	.1123	.0352	-.0683	-.0719
" " (4)	.03808	.1960	.0475	-.1031	-.1067
" " (5)	.08110	.2844	.0532	-.1195	-.1231
" " (6)	.12421	.3529	.0535	-.1204	-.1240

BaCl₂ at 44.4°C.

Acid form			[-.4010]		
Base form			+.2757		
Stock solution		.0185	+.0112	[.0000]	-.0036
Salt addition(1)	.00026	.0336	.0168	-.0147	-.0183
" " (2)	.00101	.0581	.0242	-.0352	-.0388
" " (3)	.00439	.1162	.0399	-.0789	-.0825
" " (4)	.01301	.1985	.0527	-.1155	-.1191
" " (5)	.02770	.2889	.0596	-.1357	-.1393
" " (6)	.04302	.3597	.0615	-.1416	-.1452

Na₂SO₄ at 44.5°C.

Acid form			[-.4011]		
Base form			+.2756		
Stock solution		.0185	+.0113	[.0000]	-.0036
Salt addition(1)	.00043	.0404	.0273	-.0437	-.0473
" " (2)	.00206	.0807	.0637	-.1479	-.1515
" " (3)	.00595	.1349	.1072	-.2866	-.2902
" " (4)	.01519	.2143	.1529	-.4615	-.4651
" " (5)	.02670	.2836	.1784	-.5822	-.5858
" " (6)	.04404	.3640	.1971	-.6888	-.6924

Na₂SO₄ at 44.4°C.

Acid form			[-.3997]		
Base form			+.2770		
Stock solution		.0185	+.0109	[.0000]	-.0036
Salt addition(1)	.00046	.0417	.0282	-.0471	-.0507
" " (2)	.00164	.0725	.0556	-.1248	-.1284
" " (3)	.00520	.1263	.1011	-.2660	-.2696
" " (4)	.01423	.2074	.1503	-.4492	-.4528
" " (5)	.02500	.2745	.1762	-.5685	-.5721
" " (6)	.04267	.3583	.1965	-.6812	-.6848

TABLE 4 - Continued

Solution Observed	Molality of Salt	$\mu^{1/2}$	Log (I/I _r)	Log (R ₀ /R)	Log R ₀ /R Ref. Point $\mu^{1/2} = .0150$
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NaCl at 54.6°C.

Acid form			[-.5190]		
Base form			+.4204		
Stock solution		.0187	+.0073	[.0000]	-.0037
Salt addition(1)	.00106	.0375	.0166	-.0173.	-.0210
" " (2)	.00382	.0646	.0276	-.0384	-.0421
" " (3)	.01123	.1076	.0429	-.0674	-.0711
" " (4)	.03810	.1961	.0623	-.1053	-.1091
" " (5)	.08369	.2899	.0725	-.1253	-.1290
" " (6)	.12661	.3564	.0732	-.1265	-.1302

BaCl₂ at 54.6°C.

Acid form			[-.5230]		
Base form			+.4204]		
Stock solution		.0187	+.0077	[.0000]	-.0037
Salt addition(1)	.00029	.0348	.0148	-.0130	-.0167
" " (2)	.00111	.0607	.0253	-.0332	-.0369
" " (3)	.00422	.1140	.0452	-.0709	-.0746
" " (4)	.01289	.1975	.0653	-.1101	-.1138
" " (5)	.02727	.2866	.0766	-.1323	-.1360
" " (6)	.04239	.3571	.0811	-.1412	-.1449

Na₂SO₄ at 54.6°C.

Acid form			[-.5190]		
Base form			+.4230		
Stock solution		.0187	+.0075	[.0000]	-.0037
Salt addition(1)	.00037	.0382	.0327	-.0473	-.0510
" " (2)	.00197	.0791	.0951	-.1697	-.1734
" " (3)	.00583	.1336	.1730	-.3394	-.3431
" " (4)	.01538	.2156	.2507	-.5472	-.5509
" " (5)	.02692	.2848	.2900	-.6813	-.6850
" " (6)	.04405	.3340	.3178	-.7978	-.8015

Na₂SO₄ at 54.4°C.

Acid form			[-.5000]		
Base form			+.2343		
Stock solution		.0192	-.0127	[.0000]	-.0042
Salt addition(1)	.00050	.0432	+.0079	-.0557	-.0599
" " (2)	.00220	.0835	.0513	-.1838	-.1880
" " (3)	.00566	.1317	.0953	-.3367	-.3409
" " (4)	.01494	.2126	.1410	-.5419	-.5461
" " (5)	.02570	.2783	.1628	-.6714	-.6756
" " (6)	.04173	.3543	.1777	-.7831	-.7873

Measurements are not reported for higher temperatures because a test at 65°C. revealed a small but definite fading of the indicator solution during a period of an hour. Further work is needed to determine whether suitable procedures, or possibly another indicator, will permit measurements at 65°C. or higher.

The values of K obtained from the extrapolations shown in Figure 1 appear in Table 5. It was found that the experimental results could be closely represented by empirical equations of the form,

$$\text{Log } K = A - B/T - C \text{ Log } T \quad (25)$$

Such an equation, which implies a constant ΔC_p for the ionization process, is thermodynamically plausible; it is also convenient in that ΔH° and ΔC_p° may be obtained simply from the constants B and C. The equation adopted for the ionization constants derived from investigation of sodium chloride and sodium sulfate was

$$\text{Log } K = 61.378 - 1857.1/T - 23.093 \log T \quad (26)$$

That for the series employing barium chloride as a standard neutral salt was

$$\text{Log } K = 77.5486 - 2551.8/T - 28.6778 \log T \quad (27)$$

The coefficients of $\log T$ given above correspond to $\Delta C_p^\circ = 45.9$ calories for the NaCl series, and $\Delta C_p^\circ = 57$ calories for the BaCl_2 standard. Values of K computed from these equations appear in Table 5, which presents the separate values of K obtained by extrapolation from measurements by two observers, and the mean of the individual values. The same data are presented graphically in Figure 4, in which the plotted points represent averaged experimental values, and the smooth curves equations 26 and 27.

In Table 6 are presented the values calculated from these equations at rounded 10° intervals for K, ΔH° , ΔF° , and ΔS° of the reaction



TABLE 5 - IONIZATION CONSTANTS OF THE HSO_4^- ION, $5^\circ - 55^\circ\text{C}$.

Temperature $^\circ\text{C}$	K Observed (1)	K Observed (2)	K Observed Average	K Calculated
NaCl as Reference Salt; K Calculated from Equation 26				
4.7°	.0180 ₀	.0182 ₅	.0181 ₃	.0181 ₄
14.95°	.0134 ₅	.0137 ₀	.0135 ₈	.0135 ₉
24.9°	.0101 ₈	.0101 ₃	.0101 ₈	.0101 ₈
34.9°C .	.0075 ₆	.0078 ₃	.0077 ₀	.0075 ₇
44.45°C .	.0057 ₀	.0056 ₆	.0056 ₈	.0056 ₈
54.6°C .	.0041 ₈	.0041 ₆	.0041 ₇	.0041 ₇

BaCl ₂ as Reference Salt; K Calculated from Equation 27				
4.7°	.0190 ₅	.0194 ₅	.0192 ₅	.0190 ₉
14.95°	.0138 ₅	.0142 ₅	.0140 ₅	.0143 ₃
24.9°	.0107 ₈	.0107 ₃	.0107 ₈	.0106 ₉
34.9°C .	.0077 ₇	.0080 ₇	.0079 ₂	.0078 ₇
44.45°C .	.0058 ₈	.0058 ₅	.0058 ₇	.0058 ₂
54.6°C .	.0041 ₅	.0041 ₃	.0041 ₄	.0041 ₉

TABLE 6 - THERMODYNAMIC PROPERTIES

Temperature	K Calc.	ΔH° Calc.	ΔF°	ΔS°
NaCl as Reference Salt				
5°	.0179 ₇	-4270.	2222.	-23.34
15°	.0135 ₇	-4729.	2463.	-24.96
25°	.0101 ₅	-5188.	2721.	-26.52
35°	.0075 ₅	-5647.	2993.	-28.03
45°	.0055 ₈	-6106.	3281.	-29.50
55°	.0041 ₂	-6565.	3583.	-30.92
BaCl ₂ as Reference Salt				
5°	.0189 ₄	-4179.	2193.	-22.90
15°	.0143 ₂	-4749.	2432.	-24.92
25°	.0106 ₅	-5319.	2692.	-26.86
35°	.0078 ₅	-5889.	2969.	-28.74
45°	.0057 ₂	-6459.	3266.	-30.56
55°	.0041 ₃	-7029.	3581.	-32.32

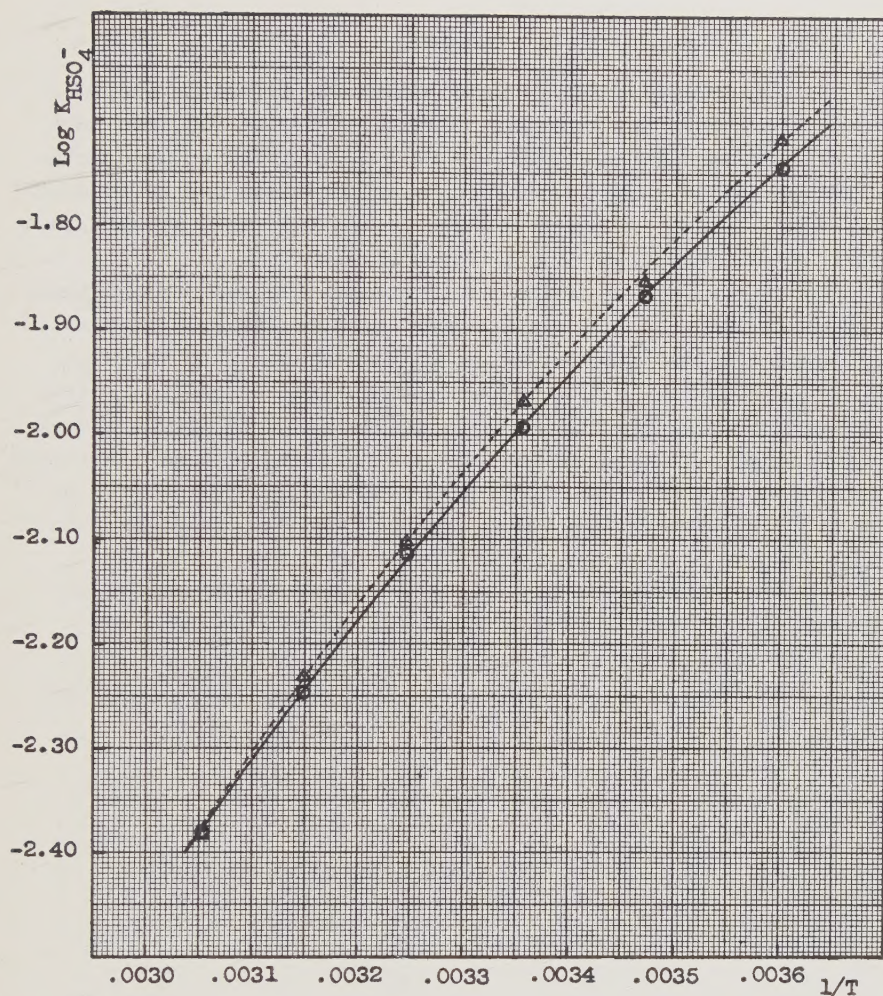


Fig. 4.--Log $K_{\text{HSO}_4^-}$ Versus $1/T$

o Log $K_{\text{HSO}_4^-}$ (average) with sodium chloride as reference salt

Δ Log $K_{\text{HSO}_4^-}$ (average) with barium chloride as reference salt

— Log $K_{\text{HSO}_4^-} = 61.378 - 1857.1 \, 1/T + 23.093 \log T$

---- Log $K_{\text{HSO}_4^-} = 77.5486 - 2551.8 \, 1/T - 28.6778 \log T$

SUMMARY

By the use of a precision indicator method developed in this laboratory, the ionization constants of the HSO_4^- ion have been determined at 10° intervals from 5° to 55°C . with an error which is probably less than 2%. These constants may be in error by as much as six per cent because of specific salt effects, but any larger error seems highly improbable.

The value obtained from these data for the heat of ionization at 25°C . is in good agreement with recent calorimetric measurements, and with the value for ΔH° derived by Noyes and Eastman from their less precise determination of the ionization constant of the HSO_4^- ion at three widely separated temperatures. Both the ionization constants and the related heats of ionization here reported are in sharp disagreement with those obtained by Hamer from electromotive force measurements. It is concluded that Hamer's results are in serious error.

For each of the temperatures studied the thermodynamic quantities ΔH° , ΔF° and ΔS° have been calculated from the change of the ionization constant with temperature. At 25°C . they have the values; $K = .0101_5$, $\Delta H^\circ = -51_{88}$, $\Delta F^\circ = 27_{21}$ and $\Delta S^\circ = 26.52$.

